View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by University of Groningen

University of Groningen

Voltage-Modulated Millimeter-Wave Spectroscopy on a Polymer Diode

Martens, H.C.F.; Hilt, O.; Brom, H.B.; Blom, P.W.M.; Huiberts, J.N.

Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.87.086601

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2001

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Martens, H. C. F., Hilt, O., Brom, H. B., Blom, P. W. M., & Huiberts, J. N. (2001). Voltage-Modulated Millimeter-Wave Spectroscopy on a Polymer Diode: Mesoscopic Charge Transport in Conjugated Polymers. Physical Review Letters, 87(8), art - 086601. [086601]. https://doi.org/10.1103/PhysRevLett.87.086601

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 12-11-2019

Voltage-Modulated Millimeter-Wave Spectroscopy on a Polymer Diode: Mesoscopic Charge Transport in Conjugated Polymers

H. C. F. Martens, O. Hilt, and H. B. Brom
Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

P. W. M. Blom
Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

J. N. Huiberts
Philips Research Laboratories, Professor Holstlaan 4 , 5656 AA Eindhoven, The Netherlands
(Received 18 December 2000; published 1 August 2001)

We present a new technique to determine the carrier mobility μ in semiconducting, undoped, conjugated polymers in the millimeter-wave frequency range, 10–500 GHz. This method probes charge conduction on mesoscopic length scales, a regime inaccessible to other transport experiments. The experiment is based on the detection of millimeter-wave absorption of field-induced charge in polymer diodes, and is applied to poly(p-phenylene vinylene). We demonstrate that locally μ can be as high as 10^{-4} m^2/Vs, and deduce the typical hopping parameters in the mesoscopic high-μ regions in the material.

DOI: 10.1103/PhysRevLett.87.086601 PACS numbers: 72.80.Le, 71.20.Rv, 73.61.Ph

Since the first report of electroluminescence in conjugated polymers [1,2] in 1990, the potential applications of polymer light-emitting diodes (PLEDs) were immediately recognized. As a result of the high external conversion efficiency (>1% photons/charge carrier) attention has been focused especially on poly(p-phenylene vinylene), PPV, and its derivatives. Today the performance of PLEDs meets many of the requirements necessary for commercial applications [3]. One of the issues that determines device performance is the transport of charge carriers. The current through PLEDs is space-charge-limited and governed by the dc hole mobility (μ_{dc}) [4,5] which, at low fields, is only 3×10^{-11} m^2/Vs at $T = 300$ K. This low mobility reflects that in the disordered PPV, the carriers are strongly localized and that charge transport proceeds by means of hopping. At high electric field strengths (E) the dc mobility follows the empirical $\ln(\mu_{dc}) \propto \sqrt{E}$ law [6], reflecting the suppression of hopping barriers in the direction of the field which exponentially enhances the hopping probability. The specific $\sqrt{E}$ dependence of $\ln(\mu_{dc})$ has been observed in a wide variety of disordered organic semiconductors [7–9], and is generally believed to arise from a heterogeneous topology of the charge-transporting sites. This heterogeneity may either arise from positive energetic correlations among adjacent transport sites [10,11], or result from structural disorder in the material [12–14]. However, these models all have in common that mesoscopic high-mobility and low-mobility regions are present, irrespective of the underlying microscopic mechanism. Recently, we demonstrated that the dc mobility of PPV is indeed well described in terms of hopping in a heterogeneous disordered system [15]: the T and E dependence of μ_{dc} can be characterized by a Gaussian site-energy distribution of width $\sigma \approx 0.1$ eV, which translates into a transport activation energy $\Delta \approx 0.5$ eV, and average transport-site separation $a \approx 1$ nm [15]. Unfortunately, as in general the dc mobility in a disordered system is limited by the weakest link in the conduction path, it cannot provide detailed insight into the transport processes involved on mesoscopic length scales.

In this Letter, we describe a new technique that allows us to study the conduction process on mesoscopic length scales in semiconducting conjugated polymers, as illustrated for PPV-based hole-only devices. The method is based on voltage-modulated millimeter-wave spectroscopy (VMS) in the frequency range $\omega/2\pi = 10$–200 GHz as a function of E and T. In general, the ac mobility $\mu(\omega)$ provides information on charge-transport processes occurring on time scales of order ω^{-1}. As demonstrated earlier for metal-insulator composites [16,17] and chemically doped polymers [18] this yields practical insight into the conduction mechanisms involved in disordered systems. Here, by applying a basic hopping formalism to the measured $\mu(\omega)$ in PPV, we are able to estimate the local hopping barriers, and to follow the evolution of the hopping times and distances in the mesoscopic high-mobility regions as a function of E.

The devices studied consist of a spin-coated layer of OC_1C_{10}-PPV [19] sandwiched between indium-tin-oxide and gold electrodes on top of a glass substrate. The polymer layer is 500 nm thick and the active area of the device is several cm^2. The current through these hole-only devices is space-charge limited [20]. The transmission of millimeter-wave radiation (10–200 GHz) through the devices is detected using a quasioptical setup as described elsewhere [21]. The diode is biased (V) and electrically modulated (δV) at frequency f_{mod} by means of a function generator in conjunction with a bipolar operational

 © 2001 The American Physical Society

amplifier. The function generator is phase locked to an ABmm millimeter-wave vector analyzer, which detects the voltage-induced change in amplitude transmission $\Delta T/T$ at the appropriate sideband. For the present experiments usually $f_{\mathrm{mod}} < 1$ kHz, which is well below the rate at which the charge density in the device can follow [22].

To appreciate the advantages of the VMS technique, it is illustrative to contrast this experiment to another powerful technique that probes high-frequency transport, the technique of time-resolved microwave conductivity (TRMC). TRMC has been applied to study radiation- or light-induced changes in conductivity of conjugated polymers [23], polymer composites [24], and polymer solutions [25], and is especially suited to examine decay kinetics. TRMC is usually performed in narrow frequency bands and, at present, cannot be applied to devices due to the strong absorption of microwave radiation by the electrodes. Furthermore, TRMC essentially probes the dynamics of the *sum* of electron density times electron mobility and hole density times hole mobility, which are all time dependent and hence may be difficult to disentangle. VMS has several important advantages: (i) it can be applied to actual device structures under operating conditions, (ii) the mobility can be unambiguously derived, since the density of field-induced carriers is exactly known, and (iii) it covers a broad frequency range which turns out to be essential for the interpretation.

The $\Delta T/T$ signal reflects the voltage-induced changes $\delta\overline{n}_1$ in the complex refractive index $\overline{n}_1 = n_1 + ik_1$, or equivalently the complex dielectric constant $\overline{\varepsilon}_1 = \overline{n}_1^2 = \varepsilon_1' - i\varepsilon_1''$, of the polymer layer. Under normal incidence, the transmission T through the polymer layer, which is sandwiched between two metallic contacts ($\overline{n}_2$), is given by

$$T = \frac{t_{21}t_{12}\exp(-i\overline{n}_1\omega d/c)}{1 - r_{21}r_{12}\exp(-2i\overline{n}_1\omega d/c)}, \qquad (1)$$

with d the thickness of the polymer, c the vacuum speed of light, and the Fresnel coefficients $t_{12} = 2\overline{n}_1/(\overline{n}_1 + \overline{n}_2)$, $t_{21} = 2\overline{n}_2/(\overline{n}_1 + \overline{n}_2)$, $r_{21} = r_{12} = (\overline{n}_1 - \overline{n}_2)/(\overline{n}_1 + \overline{n}_2)$. Neglecting spatial distribution in $\delta\overline{n}_1$ and taking into account that $|\overline{n}_2| \gg |\overline{n}_1|$ and that $|\overline{n}_1|\omega d/c \ll 1$, we obtain

$$\Delta T/T = 1 - \exp[-i\delta\overline{n}_1\omega d/c] \approx i\delta\overline{n}_1\omega d/c. \qquad (2)$$

Undoped conjugated polymers behave essentially as dielectrics, i.e., $\varepsilon_1' \gg \varepsilon_1''$, and due to the poor mobilities this holds even for high levels of carrier injection. Then $n_1 \approx \sqrt{\varepsilon_1'}$ and $k_1 \approx \varepsilon_1''/(2c\sqrt{\varepsilon_1'}) = \sigma_1'/(2\omega c\varepsilon_0\sqrt{\varepsilon_1'})$ with conductivity $\sigma_1' = \omega\varepsilon_0\varepsilon_1''$. Furthermore, for $\mu < 1$ m^2/Vs it is legitimate to neglect the influence of $\delta\varepsilon_1'$ in the present ω range [26,27]. In this case Eq. (2) simplifies to $\Delta T/T = \delta\sigma_1' d/(2c\varepsilon_0\sqrt{\varepsilon_1'})$. Changes in σ' relate to those in carrier density ($\delta\rho$) and mobility ($\delta\mu$) via

$$\delta\sigma = \delta\rho q\mu + \rho_0 q\delta\mu. \qquad (3)$$

For a space-charge limited device [20,28] the background carrier concentration $\rho_0 = V(3\varepsilon'\varepsilon_0)/(2eL^2)$, and $\delta\rho = \delta V(3\varepsilon'\varepsilon_0)/(2eL^2)$. From Eq. (3) μ is solved:

$$\mu(V) = \frac{2eL^2}{qV\delta V(3\varepsilon'\varepsilon_0)}\int_0^V \delta\sigma_1' dV'. \qquad (4)$$

We will now discuss the VMS data of OC_1C_{10}-PPV. Figure 1 shows the magnitude and accuracy of the relative change in transmission as a function of field for two frequencies. Figure 2a presents the frequency-dependent mobility in the range 10–200 GHz as a function of $E = V/L$. The mobility increases strongly with both E and ω and seems to saturate at the highest frequencies. Solid lines are fits to a model discussed below. Temperature dependent measurements have been performed at $\omega/2\pi =$ 95 GHz. In Fig. 2b the diffusion constant, which is defined as $\mu \times (k_BT/e)$, is plotted versus $1/T$ for two different bias electrical fields. The T dependence becomes less pronounced for increasing E.

The hole mobility at these high frequencies lies 6 orders of magnitude above μ_{dc} ($\sim 10^{-10}$ m^2/V s) , which is a direct manifestation of the percolative nature of transport in strongly disordered media. Figure 3a sketches a potential-energy landscape that captures the basic ingredients relevant for the transport properties of our system: the local minima represent transport sites. As a result of the heterogeneity, potential-energy valleys and barriers are present on larger, mesoscopic, length scales. Note that this model implies a spatially varying mobility; the valleys correspond to the high-mobility regions discussed above. First let us consider the case of weak bias. A carrier that is injected into the potential-energy landscape will be caught in one of the potential wells. Since hops over small barriers are *exponentially* faster than those over large barriers, effectively the carrier "bounces back and forth" in the valley as indicated by the solid arrows. Occasionally, the carrier is able to jump over the high barrier to the next potential well as shown by the dotted arrow. These "hard hops" (or sequence of hard hops) limit the dc mobility and determine its activation energy Δ. From impedance experiments [22] and a simple calculation [29] we estimate the rate of

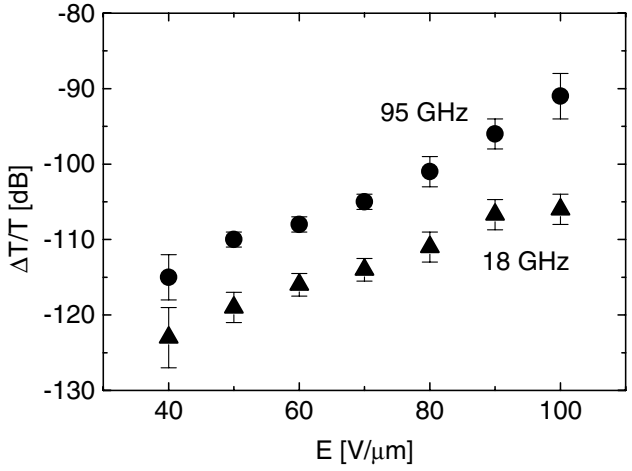

FIG. 1. Relative change in mm-wave amplitude transmission as a function of electrical field and frequency.

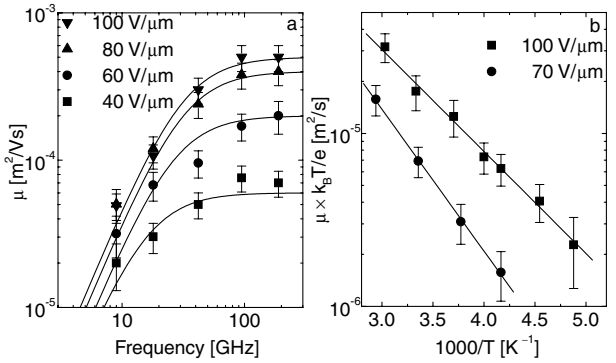

FIG. 2. (a) Frequency dependent hole mobility as a function of bias electrical field in OC_1C_{10}-PPV. Solid lines are fits to a hopping model. (b) T dependence of the high-frequency (95 GHz) diffusion constant $\mu \times k_B T/e$ as a function E. Solid lines are fits to an Arrhenius law.

these hard hops to be in the MHz regime. Hence, in the 10–200 GHz range studied here, only the fast relaxation of carriers confined to these mesoscopic high-mobility regions is probed and $\mu(\omega)$ can be calculated as follows.

Let us assign a mobility $\mu_h \gg \mu_{\rm dc}$ to a microscopic valley of size R, and assume that hops beyond R are too slow to contribute to the high-ω response. This leads to the simplified picture of a carrier performing a random walk within a confining potential well (and with equal hopping probabilities between neighboring sites); see Fig. 3c. Then, an (ac) electrical field E induces a polarization $E(eR)^2/(k_B T)$. For a constant μ_h within the valley, this polarization decays single exponentially with a characteristic time $\tau = eR^2/(\mu_h k_B T)$, and the ω-dependent response is of the Debye form

$$\mu(\omega) = \frac{eR^2}{k_B T} \, \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \, . \qquad (5)$$

For $\omega > \tau^{-1}$, $\mu(\omega) = eR^2/(k_B T \tau) = \mu_h$, i.e., only the mobility within the well is probed. The finite size of the well leads to the low-ω roll-off $\mu(\omega) \sim \omega^2$ which would become weaker if also the slower hops beyond R were taken into account. Obviously the strong ω dependence predicted by Eq. (5) and hopping models in general, implies that μ data at a single frequency may be difficult to interpret. Note that this model presupposes the carriers to be in local equilibrium. However, already for $R > 0.3$ nm (the typical hopping distances are at least 1 nm [15]) $eER > k_B T$. Nonetheless, if on time scales ω^{-1} the carriers are unable to escape from the deep valleys (confinement condition), they will be in quasiequilibrium and Eq. (5) can be applied. Since even at strong bias, the data show $\mu(\omega) \gg \mu_{\rm dc}$, demonstrating that locally fast "back and forth" hops occur, this condition apparently holds. In principle, to obtain the appropriate high frequency mobility, Eq. (5) should be averaged over the distributions in τ and R [30,31]. However, within our experimental accuracy, Eq. (5) already provides a satisfactory description of the data; see the solid lines in Fig. 2a. The derived transport parameters are presented in Fig. 4.

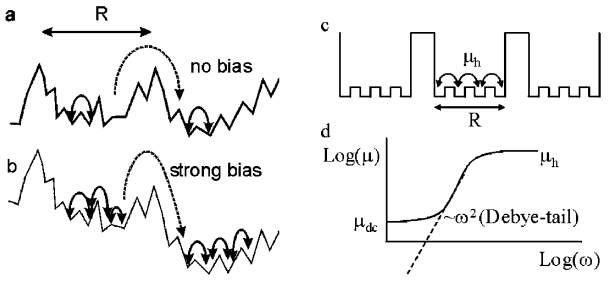

FIG. 3. Schematic representation of a heterogeneously disordered potential-energy landscape without bias (a) and with an applied bias (b). $\mu_{\rm dc}$ is limited by the hard hops over the highest potential barriers (dotted arrows). At sufficiently high frequencies conduction in the high-mobility regions (solid arrows) can be probed. In the simplified transport model for high-μ regions separated by barriers shown in (c), only a single intravalley relaxation time appears, and the ac response is given by Eq. (5) with a $\mu(\omega)$ dependence as shown in (d).

As demonstrated in Fig. 4, R increases as a function of E. To explain why this occurs, we turn again to Fig. 3. Under the application of a strong bias potential the energy landscape becomes tilted. This lowers the potential-energy barriers, which enables the carrier to partly "climb" the confining walls of the valley: even though the carrier is still unable to escape the mesoscopic high-mobility region, the size of this region effectively becomes larger. The E

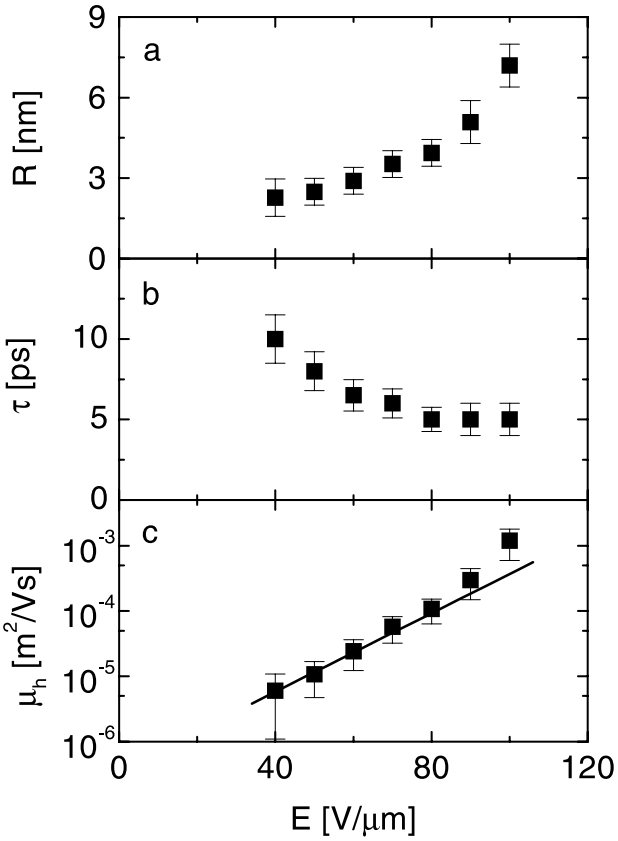

FIG. 4. Field-dependence of (a) the distance R over which carriers move relatively easily, (b) the corresponding hopping time τ, (c) the mobility $\mu_h = eR^2/(\tau k_B T)$ within the high-μ regions [drawn line represents a fit to $\ln\mu \propto eER_0/(k_B T)$].

dependence of the estimated intravalley relaxation time τ is shown in Fig. 4b. It reveals a decrease for increasing fields but seems to level off at the highest fields. Using $R(E)$ and $\tau(E)$ we find that the effective local mobility $\mu_h = eR^2/(k_B T\tau)$ strongly increases with E; see Fig. 4c. The T dependence of μ_h, Fig. 2b, implies that the transport is activated; the solid lines represent fits to an Arrhenius law with the activation energies $\Delta' = 0.15$ eV and $\Delta' = 0.12$ eV for $E = 70$ V/μm and $E = 100$ V/μm, respectively. The decrease of Δ' with increasing E reflects the barrier lowering. Extrapolation towards $E = 0$ suggests a barrier height of 0.2 eV.

What do these results imply for the transport in PPV? The activation of μ_h shows that even within the mesoscopic high-mobility regions hopping barriers of 0.2 eV are present. This is significantly lower than the 0.5 eV barriers limiting the dc transport, and accounts for a factor 10^5 increase in mobility at room temperature. According to Fig. 4, the strong E dependence of $\mu(\omega)$ results from both the larger distance over which fast hops occur, and from the higher relaxation rates: at 100 V/μm the carriers are able to traverse distances as long as 10 nm within a few ps. Since τ even weakly *decreases* while R increases at high E, the mobility within the high-μ regions is strongly enhanced by the electric field. Barrier lowering should exponentially enhance the hopping process, $\mu_h \propto \exp[eER_0/(k_B T)]$, and from the data shown in Fig. 4c we estimate $R_0 = 1.7 \pm 0.3$ nm which corresponds to about 3 monomers. Here R_0 could be loosely interpreted as the width of the 0.2 eV barriers. While we cannot be conclusive on the microscopic origin of the high-mobility regions in PPV, the presented results do corroborate the notion of disorder on mesoscopic length scales of at least 10 nm.

In the above analysis we considered only the contribution of the fastest hops to the conduction process, which we believe captures the basic features of the high-frequency mobility. At lower frequencies, relaxation via slower hops will gain weight, and this simplified model will underestimate the mobility. A deeper insight into the charge transport in semiconducting conjugated polymers could be provided by models that link the material's heterogeneous topology to the proper distributions in τ and R.

In summary, voltage-modulated millimeter-wave spectroscopy is a promising new technique to study charge transport in semiconducting conjugated polymers. Experiments have been performed from 10 to 200 GHz and are presently extended to the THz regime. For the investigated PPV, we are able to probe transport within nanometer-sized high-mobility regions where the mobility is 10^6 times higher than the dc mobility. Diffusion times across these regions, in which barriers of about 0.2 eV need to be surmounted, are on the ps time scale. Barrier lowering due to an applied electrical field both enhances the hopping rates and increases the distance over which fast carrier relaxation occurs.

Discussions with G. W. 't Hooft, M. Bonn, J. van Bentum, and P. Goy are gratefully acknowledged. This work is part of the research programme of FOM-NWO.

[1] J. H. Burroughes *et al.,* Nature (London) **347**, 539 (1990).
[2] D. Braun and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991).
[3] R. H. Friend *et al.,* Nature (London) **397**, 121 (1999).
[4] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
[5] H. C. F. Martens *et al.,* Phys. Rev. B **63**, 125328 (2001).
[6] P. W. M. Blom, M. J. M. de Jong, and M. G. van Munster, Phys. Rev. B **55**, R656 (1997).
[7] D. M. Pai, J. Chem. Phys. **52**, 2285 (1970).
[8] L. B. Schein, A. Peled, and D. Glatz, J. Appl. Phys. **66**, 686 (1989).
[9] P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Imaging Systems* (Dekker, New York, 1993).
[10] S. V. Novikov *et al.,* Phys. Rev. Lett. **81**, 4472 (1998).
[11] Z. G. Yu *et al.,* Phys. Rev. Lett. **84**, 721 (2000).
[12] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[13] S. V. Rakhmanova and E. M. Conwell, Appl. Phys. Lett. **76**, 3822 (2000).
[14] P. W. M. Blom and M. C. J. M. Vissenberg, Mater. Sci. Eng. **R27**, 53 (2000).
[15] H. C. F. Martens, P. W. M. Blom, and H. F. M. Schoo, Phys. Rev. B **61**, 7489 (2000).
[16] L. J. Adriaanse *et al.,* Phys. Rev. Lett. **78**, 1755 (1997).
[17] J. A. Reedijk, H. B. Brom, L. J. de Jongh, and G. Schmid, Phys. Rev. B **57**, R15116 (1998).
[18] J. A. Reedijk, H. C. F. Martens, H. B. Brom, and M. A. J. Michels, Phys. Rev. Lett. **83**, 3904 (1999).
[19] D. Braun *et al.,* Synth. Met. **66**, 75 (1994).
[20] Current-voltage characteristics were similar to those of other devices prepared in the same way, and for which space-charge-limited currents are well established [4–6].
[21] J. A. Reedijk, H. C. F. Martens, B. J. G. Smits, and H. B. Brom, Rev. Sci. Instrum. **71**, 478 (2000).
[22] H. C. F. Martens, H. B. Brom, and P. W. M. Blom, Phys. Rev. B **60**, R8489 (1999).
[23] M. P. de Haas *et al.,* Synth. Met. **101**, 524 (1998).
[24] J. S. Salafsky, W. H. Lubberhuizen, and R. E. I. Schropp, Chem. Phys. Lett. **290**, 297 (1998).
[25] R. J. O. M. Hoofman, M. P. de Haas, L. D. A. Siebbeles, and J. M. Warman, Nature (London) **392**, 54 (1998).
[26] S. Grabtchak and M. Cocivera, Phys. Rev. B **58**, 4701 (1998).
[27] Since dipolar contributions to ε' in general are limited to the sub-GHz regime and for the specific OC_1C_{10}-PPV studied here even the sub-MHz regime [22], electrostriction will not contribute to the GHz response.
[28] M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970).
[29] Since $\Delta \approx 0.4$–0.5 eV [6], the rate of the "hard" hops is $\nu_{\mathrm{ph}} \exp(-\Delta/k_B T) \approx 10^6\ \mathrm{s}^{-1}$ with $\nu_{\mathrm{ph}} \approx 10^{13}\ \mathrm{s}^{-1}$ the phonon-assisted hopping attempt-frequency.
[30] M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961).
[31] A. Bello, E. Laredo, and M. Grimau, Phys. Rev. B **60**, 12 764 (1999).